

PEROVSKITE $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ SOLAR CELLS AND THEIR DEGRADATION (PART 1: A SHORT REVIEW)

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Development of hybrid organic-inorganic perovskite solar cells (PSC) has been one of the hottest research topics since 2013. Within brief literature review, we would like to achieve two objectives. Firstly, we would like to indicate that a whole set of physical properties, such as high charge carrier mobility, very low recombination rates, large carrier life time and diffusion length, large absorption coefficients and very weak exciton binding energies, are defining high power conversion efficiency (PCE) of methyl ammonium lead trihalide SC. The second objective is to draw attention to some, in our opinion, important aspects that previously have not been satisfactory addressed in literature. Although degradation of PSC is widely discussed, processes at very first exposure to ambient conditions after deposition of top electrode are uncovered.

Keywords: *Inverted solar cells, lead halide perovskite, power conversion efficiency.*

1. INTRODUCTION

Due to the increasing demand for clean energy, much research effort has been dedicated to the improvement of solar energy technologies. As a result, in 2013 Grätzel's group created a mesoporous hybrid organic-

inorganic perovskite solar cell (PSC) with certified power conversion efficiency (PCE) of 15 % [1]. At the same time, Snaith's group also succeeded in creating a planar organic-inorganic perovskite solar cell with PCE of

15.4 % [2]. In the prominent scientific journal “Nature”, these PSCs were described as one of the ten greatest scientific achievements of 2013 [3]. Since the time of these achievements, the research into PSCs has grown rapidly, which has been described as a “perovskite fever” [4], and in 2019 the efficiency of the PSCs reached 24.2 % [5].

These astonishing efficiencies are attributed to the very interesting electronic and optical properties of the perovskite layer [6]–[13]. The most studied compound for the perovskite solar cells is methyl ammonium lead triiodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$). It has a charge carrier mobility of $8 \text{ cm}^2/(\text{V}\cdot\text{s})$ in thin polycrystalline layers [6], but this quantity is much higher for monocrystals, reaching $105\pm 35 \text{ cm}^2/(\text{V}\cdot\text{s})$ [13]. These perovskites also have extremely low charge carrier recombination rates for both the monomolecular and the bimo-

lecular recombinations [6]. In addition, they feature an ambipolar charge transport with a balanced electron and hole diffusion lengths, these being greater than 100 nanometers in a polycrystalline $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer [14], [15]. In monocrystals, though, the electron and the hole diffusion lengths exceed $175 \mu\text{m}$ under illumination of nominal full sunlight intensity and even 3 mm under 1000 times weaker illumination [13]. The aforementioned features of trihalide perovskites provide long lifetime of photogenerated charge carriers [6], [11], [14], [16]. These perovskites have a broad absorption spectrum covering all the visible range up to 800 nm on the red side, with a high absorption coefficient from $5\cdot 10^4$ up to $5\cdot 10^5 \text{ cm}^{-1}$ [17]–[20]. Commonly, a thickness of $300\div 400 \text{ nm}$ is sufficient for such a perovskite to fully absorb the incident visible light [18], [21], [22].

2. DISCUSSION

It is possible to create exceptionally thin solar cells with a record power-per-weight figure of merit of $23 \text{ W}\cdot\text{g}^{-1}$ [22], which was never achieved by any other competing photovoltaic technologies. Another advantage is the low fabrication cost of such solar cells, “because material cost of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ absorber (300 nm thick) is less than US\$ 2 per square meter and the coating processes are very simple” [18]. These cells do not have excitonic nature, unlike the organic solar cells, but rather have photoexcitations spontaneously dissociating into free carriers in the bulk of the junction, as in the inorganic cells [23]. This characteristic is determined by the very small exciton binding energy of $\sim 2 \text{ meV}$ [24] and high static dielectric constant $\epsilon \sim 70$ [24]. These very low exciton binding energy values were also confirmed by other

groups, namely, 6 meV [25], [26] at the room temperature for high-quality metal-organic triiodide perovskite layers obtained by the interdiffusion method; a somewhat higher value of $\sim 22\div 24 \text{ meV}$ was found by optical spectroscopy using Elliott analysis [27]. This explains the very impressive performance of the metal-organic perovskite solar cells: following the absorption of the light, the free charge carriers are generated spontaneously.

Although the triiodide perovskites are the most widely investigated ones, usage of a mixed halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ as light absorber has some advantages, as it has much higher charge carrier mobilities and diffusion lengths even in polycrystalline layers (up to $1 \mu\text{m}$, which is an order of magnitude higher than for the pure iodide perovskite) [11]. The Cl^- presence in the

perovskite precursor solution improves the layer crystallization and increases the charge carrier lifetime up to $1\mu\text{s}$ [12], [20]. The mixed halide perovskites also have higher PCE values and are more stable [28]. Despite the content of chlorine in the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ is very small and x does not exceed $2\div 4\%$ [12], [20], [29], it decreases concentration of the bulk traps by about an order of magnitude compared to the $\text{CH}_3\text{NH}_3\text{PbI}_3$ [30], [31]. The chlorine additive alters the direction of the grain growth for perovskite layers formed from the precursor solution in DMF on PEDOT:PSS-covered indium-tin oxide (ITO) glass, so that the $\text{CH}_3\text{NH}_3\text{PbI}_3$ forms a fibrous structure with a low surface coverage, whereas the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ tends to crystallize in a planar fashion with a practically complete substrate coverage [30].

Another option for obtaining the highest power conversion efficiencies is mesoporous bulk heterojunction cells; these, however, typically contain expensive charge-transport-and-blocking layers, which need high-temperature ($400\div 500^\circ\text{C}$) [32]–[34] sintering, thus increasing the processing time and the cost of the solar cell. To overcome these drawbacks, a low-temperature-processed inverted planar p|i|n solar cell could be produced using poly(3,4-ethylenedioxythiophene) poly(styrenesulphonate) (PEDOT:PSS) as the hole-transport (p) and electron-blocking layer material, while the phenyl- C_{61} -butyric acid methyl ester (PCBM or, more specifically, PC_{61}BM) is employed in the electron transport (n) layer (ETL), as frequently done in the design of planar inverted hybrid solar cells [28], [35], [44]–[46], [36]–[43]. These charge-carrier transport layers are also applicable to the low-cost printable or roll-to-roll manufacturing solar cells [47].

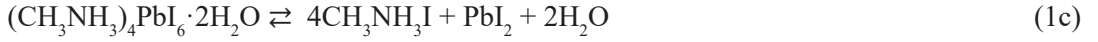
Usually after PCBM is spin-coated onto a perovskite film, the traps are efficiently

passivated and their density in the cell is decreased by nearly two orders of magnitude within the $0.4\div 0.5\text{ eV}$ range; photocurrent hysteresis is also diminished [48], [49]. The shallow trap states in the $0.35\div 0.40\text{ eV}$ range, however, are passivated only after thermal annealing of the PCBM layer for 45 min at 100°C [48]. The hole mobility in the plane direction has also been reported to increase up to $114\text{ cm}^2/(\text{V}\cdot\text{s})$ for a polycrystalline perovskite film covered by PCBM layer [48]. This means that after thermal annealing, the PCBM diffuses into the perovskite layer along the grain boundaries, passivating the shallow trap states there and reducing the energy barrier between the grains, which enhances the hole transport in the plane direction [48]. Even better trap passivation has been achieved when the PCBM layer is covered with a C_{60} layer. Such a bilayer ETL can passivate not only the shallow trap states but also the ones deeper than 0.5 eV [50], and it also reduces the dark current by $3\div 4$ orders of magnitude.

Despite the attractive performance and the low fabrication cost of organic-inorganic perovskite solar cells, the long-term stability is a major drawback hindering their practical application [28], [44], [51]–[57]. These cells degrade rapidly under humid air, sunlight and heat [51]–[58]. Among these causes, humidity is the main as it significantly amplifies the degradation speed of the cell under oxygen, light and temperature after reaching a threshold of $2\cdot 10^{10}$ langmuir of water vapour exposure [58]–[60]. It was shown that moisture permeates into the polycrystalline perovskite MAPbI_3 layer through the grain boundaries much more quickly than reacts with the grain top surface, as the grain boundaries consist of a $\sim 5\text{ nm}$ thick amorphous intergranular film [61]. The degradation process proceeds in two stages. At first, the perovskite mono-

hydrate $\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{H}_2\text{O}$ and also the mixed dihydrate are formed, which are fully reversible reactions, the direction of which

depends on the water vapour concentration in air [53, 57, 60, 61]:



However, with additional moisture and time, especially the dihydrate can decompose into CH_3NH_2 , PbI_2 , HI , I_2 and H_2O , which is irreversible due to the volatility of many of these products [53]. The degradation process can be slowed down by choosing appropriate charge transport layers [44].

In case when a bilayer ETL of the PCBM/ C_{60} is used, not only passivation of the trap states takes place, but also the hysteresis diminishes and the cell humidity stability improves due to the hydrophobic nature of the PCBM top layer in the inverted cell [37]. Another option how to slow down degradation could be making the top electrode thick enough. However, at the present time it is difficult to find data in literature on how the top electrode thickness influences cell degradation during its exposure to ambient air after thermal deposition of the top electrode.

As far as we know, there is only one study in literature, which considers the pres-

sure influence upon the solar cell parameters [62]; yet its authors have investigated only the open-circuit voltage (V_{oc}) change kinetics in vacuum and only for a direct mesoporous pure-triiodide perovskite cell. Similar investigations for the inverted planar mixed halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ cell, to our knowledge, have not been reported.

Most studies involve only determining the spectral dependence of the short-circuit photocurrent (SCP) EQE (see, for example, [1], [37], [63]), but it is not always possible to reliably describe the cell response to varying external factors by acquiring of just this single parameter. Therefore, additional spectral dependencies for the fill factor (FF), V_{oc} and the power conversion efficiency (PCE) determined before and after the cell exposure to air could be useful to describe the first steps of degradation. We have not found such a type of cell characterisation reported in the literature.

3. CONCLUSION

1. The main physical parameters concerning high change carrier mobility, very low recombination rates, large carrier life time and diffusion length, large absorption coefficients

and very weak exciton binding energies have been reported to explain very impressive performance of organic-inorganic perovskite solar cells.

- Literature analysis has shown that adding a small amount of Cl⁻ ions in Pb triiodide perovskite (mixed halide perovskite cells) has a favourable effect on the above-mentioned physical parameters.
- Employing the double electron transport layer (ETL) PCBM/C₆₀ is beneficiary because it is clearly evident that such ETL passivates the shallow and also deep trap states and diminishes hysteresis. Double ETL also improves the cell humidity stability by its hydrophobic nature. These observations demonstrate how important is to choose hydrophobic character charge carrier transport layers to diminish the cell degradation processes.
- To get a deeper insight into organic-inorganic perovskite solar cell degradation processes, it would be valuable to study spectral dependencies of FF and Voc. This could provide valuable information about cell PCE spectral changes under degradation as well as better understanding of what occurs with charge carrier recombination processes and possible hot carrier participation.

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